High-Field Magnetization of a Quasi-One-Dimensional $S=1$ Antiferromagnet $Ni(C_2H_8N_2)_2NO_2(ClO_4)$: Observation of the Haldane Gap

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High-field magnetization measurements were performed for the quasi-one-dimensional $S=1$ antiferromagnet $Ni(C_2H_8N_2)_2NO_2(ClO_4)$ up to 39 T. Applied magnetic fields parallel and perpendicular to the chain axis induce a transition from the nonmagnetic to the magnetic state at a critical field, $H_c^{\parallel}=9.8$ T and $H_c^{\perp}=13.1$ T, indicating clear evidence for the existence of the Haldane gap. The observed gaps are markedly different from those in neutron-scattering experiments.

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Haldane[1] has predicted the existence of a quantum energy gap between the singlet ground state and the lowest excited state in a one-dimensional Heisenberg antiferromagnet (1D HAF) with integer spin. After some controversy this prediction has been verified by numerical simulations[2,3] and by rigorous proof for a solvable model.[4] The first experimental evidence for the Haldane gap was given by Buyers *et al.*[5] and subsequently by Steiner *et al.*[6] from inelastic neutron-scattering experiments of $CsNiCl_3$. Renard *et al.*,[7] however, pointed out that $CsNiCl_3$ is far from the best candidate for a model substance to test the Haldane gap since the relatively large interchain interaction ($J'/J=10^{-2}$) induces a long-range order at $T_N=4.85$ K. They suggested that an organic crystal $Ni(C_2H_8N_2)_2NO_2ClO_4$, abbreviated to NENP by them, is a much better system of a nearly ideal $S=1$ 1D HAF having a large intrachain interaction ($J/k\simeq 50$ K), a small anisotropy ($D/k\simeq 1$ K), and a small interchain interaction. In fact, no 3D long-range order has been observed down to 1.2 K. They concluded[8] that the observed gaps for the longitudinal and transverse excitations, $E_G^{\parallel}\simeq 30$ K and $E_G^{\perp}\simeq 14$ K, result from the splitting of the Haldane gap of the pure Heisenberg chain given by $E_{G0}=(E_G^{\parallel}+E_G^{\perp})/2\simeq 22$ K, in the presence of the large planar anisotropy $D\simeq 10$ K.

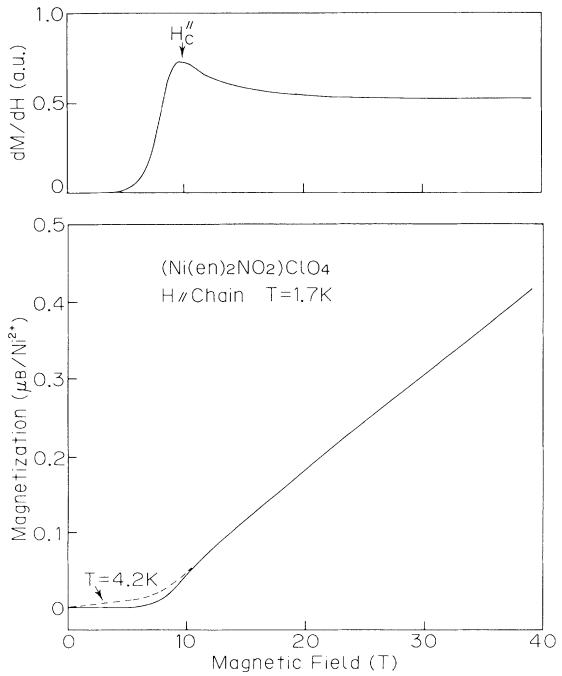

FIG. 1. Magnetization M and the field-derivative dM/dH curves in the magnetic field applied parallel to the chain axis. The critical field $H_c^{\parallel}$ is indicated by an arrow in the top figure.

The aim of the present study is to observe a gap in NENP by the high-field magnetization measurement. The appearance of a gap between the singlet ground state and the lowest excited triplet state results in zero susceptibility at low temperatures. The application of a strong magnetic field is expected to induce a finite susceptibility at some critical field corresponding to the gap energy as a result of level crossing between the ground state and the excited state. A preliminary report for a powder sample has shown an interesting behavior.[8]

High-field magnetization curves of the single-crystal NENP were measured at constant temperatures 4.2 and 1.7 K in high magnetic fields up to 39 T applied parallel and perpendicular to the chain axis. The measurement was made using an induction method with a multilayer pulse magnet at the Ultra-High Magnetic Field Laboratory, Institute for Solid State Physics, Tokyo. The sample was prepared using a known procedure.[9] The single crystals were cut into rods, 3 mm in diam and 10 mm in length, to fit a signal pickup coil.

Figures 1 and 2 show the magnetization curves in magnetic fields up to 39 T applied parallel and perpendicular to the chain axis, respectively. The field-derivative curves of magnetization dM/dH are also plotted. The results clearly prove the existence of an energy gap between the nonmagnetic ground state and the magnetic excited state. We note four remarkable features in these figures. (i) Data for both the parallel and perpendicular fields exhibit a definite anomaly of magnetization

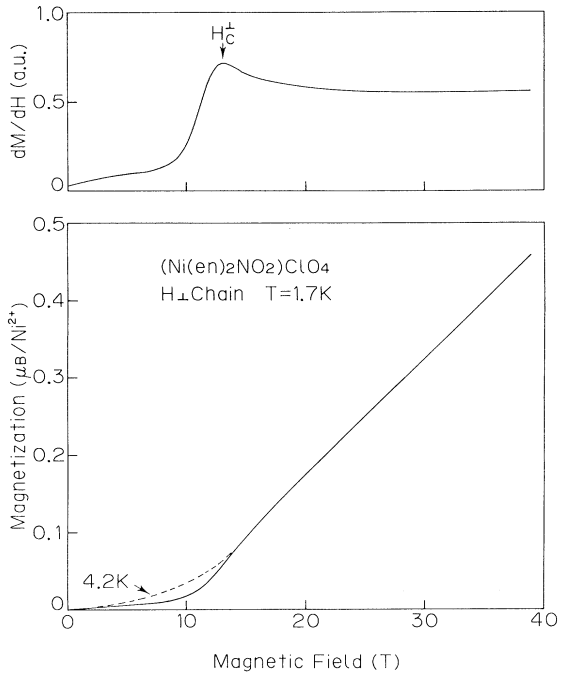

FIG. 2. Magnetization M and the field-derivative dM/dH curves in the magnetic field applied perpendicular to the chain axis. The critical field $H_c^\perp$ is indicated by an arrow in the top figure.

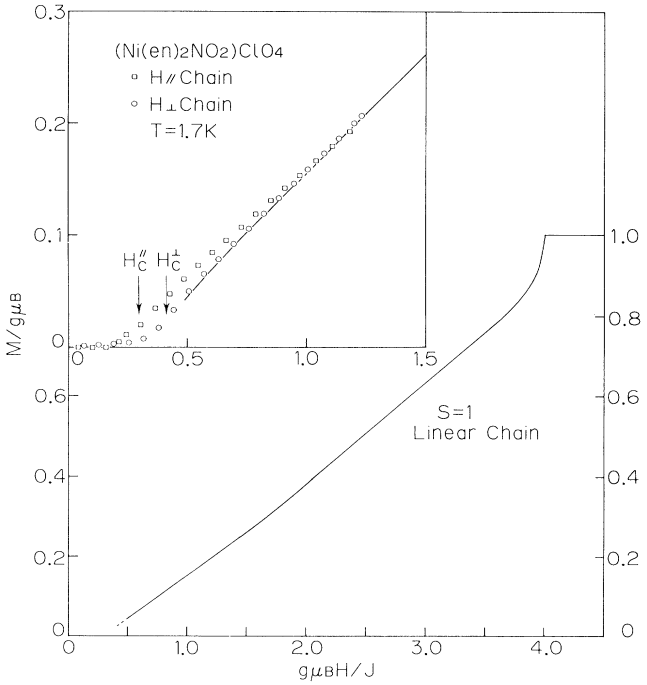

FIG. 3. The theoretical magnetization isotherm at $T=0$ K for $S=1$ 1D HAF. Inset: Comparison of the observed magnetization data with the calculation. The fitting parameters are $J=47$ K, $g_\parallel=2.15$, and $g_\perp=2.22$. Excellent agreement can be seen for the data in the high-field region above the critical field. The experimental data are depicted in a discrete manner for clarity.

at a critical field defined by the field at which dM/dH is maximum. Values of the critical field for both directions, $H_c^\parallel=9.8$ T and $H_c^\perp=13.1$ T, are markedly different from each other, implying the existence of an anisotropic term in the energy gap. (ii) The observed magnetization curves do not show an abrupt jump, but an inflection at the critical field as is clearly seen in the dM/dH curves, suggesting that this anomaly is not associated with the first-order transition. (iii) The temperature dependence is appreciable only below the critical field H_c, and the induced magnetization below H_c increases with increasing temperature, indicating a thermal activation to the magnetic excited state. (iv) The susceptibility at low field is practically zero for the parallel direction, but finite for the perpendicular direction. This indicates the presence of an off-diagonal contribution to the perpendicular magnetization, which is reminiscent of a non-negligible single-ion anisotropy.

From the observed critical fields, $H_c^\parallel=9.8$ T and $H_c^\perp=13.1$ T, we can estimate the energy gap, $E_G^\parallel=g_\parallel\mu_B S H_c^\parallel=14.2$ K and $E_G^\perp=g_\perp\mu_B S H_c^\perp=19.5$ K, for parallel and perpendicular directions to the chain axis, using $g_\parallel=2.15$, $g_\perp=2.22$, and $S=1$. These values of the energy gap are compared favorably with $E_G^\parallel=11$ K and $E_G^\perp=17$ K estimated from the low-temperature susceptibility data below 5 K.[7] This fact implies that the effective energy gap $E_G(H)$ under the magnetic field can be expressed for both directions by the simple relation,

$$E_G^{\parallel,\perp}(H)=E_G^{\parallel,\perp}-g_{\parallel,\perp}\mu_B S H . \quad (1)$$

The effective gap is field dependent and the energy gap closes at $H_c^\parallel$ and $H_c^\perp$.

Parkinson and Bonner[3] performed numerical calculations of the magnetization for 1D HAF. As shown in Fig. 3, the observed magnetization data are in excellent agreement with the extrapolated magnetization isotherm at $T=0$ K for $S=1$ 1D HAF which is believed to be exact except for the low-field region where the extrapolation is not completed. The fitting parameters used are $J=47$ K, $g_\parallel=2.15$, and $g_\perp=2.22$. We found that the low-field magnetization curve below the critical field can be expressed by an exponential function, $M \propto \exp[-E_G(H)/kT]$, as shown in Fig. 4. The fact indicates that the energy gap is given by Eq. (1). We notice a crossover phenomenon in the temperature dependence. The observed strong temperature dependence below H_c is caused by this exponential dependence. The ratio

$$\exp[-E_G(H)/4.2\text{ K}]/\exp[-E_G(H)/1.7\text{ K}]$$

is of the order of 10 to 50 depending on H. Above H_c, however, the vanishing gap results in nearly temperature-independent finite susceptibility at low temper-

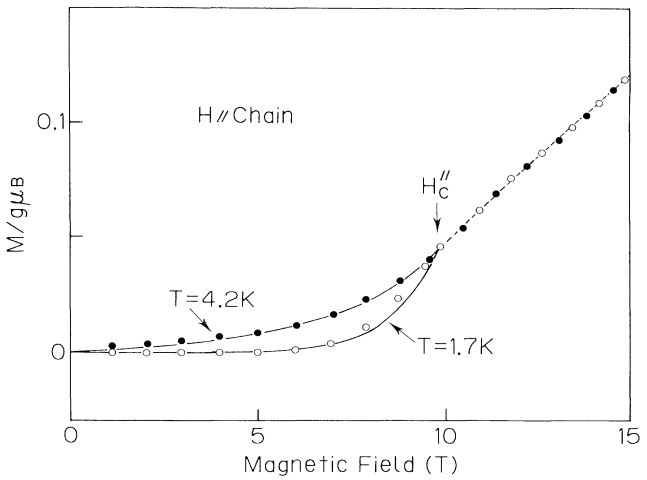

FIG. 4. Enlarged figure of the magnetization curve for $H \parallel$ chain in the low-field region. The solid curves below H_c represent the exponential dependence, $M \propto \exp[-E_G(H)/kT]$, and are smoothly connected with the magnetization isotherm at $T=0$ K for $S=1$ 1D HAF at $H_c^{\parallel}$. The experimental data are depicted in a discrete manner for clarity.

ature. The temperature effect is now scaled by J instead of E_G. The scaled temperatures, 1.7 K/J = 0.034 and 4.2 K/J = 0.084 with J = 50 K, are sufficiently low to apply the $T=0$ K magnetization isotherm.

It should be noted that the energy gaps determined by the present experiment, $E_G^{\parallel}=14.2$ K and $E_G^{\perp}=19.5$ K, are different from those by neutron scattering, $E_G^{\parallel}=30$ K and $E_G^{\perp}=14$ K, and the relative values are opposite each other. More interestingly, our measurements show that the gap closes at H_c, while neutron scattering reveals that the gap is nearly independent of the field up to H_c.[8] These discrepancies are considered to be due to the different behavior of the energy gap at the zone center ($k=0$) and at the boundary ($k=\pi$). This means that the excitation spectrum in NENP is asymmetric about $k=\pi/2$.

At present there exists no theory to describe the energy gap including the effect of the single-ion anisotropy. We propose a heuristic formula to satisfy the present results and those of the neutron scattering as follows:

$$E_G(k,\theta) = (J/2)(1+\alpha\cos k) - D(\cos^2\theta\cos k+\sin^2\theta/2)\,, \quad (2)$$

where α is the numerical constant, D is the single-ion anisotropy constant, and θ is the angle of the spin polarization from the c axis. The first term corresponds to the isotropic energy gap and its k dependence is essentially the same as $E_G(k)$ predicted by Arovas, Auerbach, and Haldane[10] except for the numerical constant. The second term corresponds to the anisotropic gap consisting of parallel and perpendicular contributions.

For $k=\pi$, Eq. (2) yields

$$E_G(\pi,\parallel) = (J/2)(1-\alpha)+D \quad (3)$$

and

$$E_G(\pi,\perp) = (J/2)(1-\alpha)-D/2\,. \quad (4)$$

Equations (3) and (4) are consistent with the numerical result[2] near the Heisenberg point (see Fig. 13 in Ref. 2). The isotropic gap is not given by $E_{G0}=[E_G(\pi,\parallel)+E_G(\pi,\perp)]/2$, but by $[E_G(\pi,\parallel)+2E_G(\pi,\perp)]/3$. The physical meaning is rather transparent in view of the fact that in the presence of the anisotropy the excited triplet of the isotropic chain splits into a doubly degenerate "transverse mode" and a "longitudinal mode" from a massive excitation point of view.[1,4]

For $k=0$, Eq. (2) yields

$$E_G(0,\parallel) = (J/2)(1+\alpha)-D \quad (5)$$

and

$$E_G(0,\perp) = (J/2)(1+\alpha)-D/2\,. \quad (6)$$

We assign the gaps observed from the neutron scattering (NS) and the present experiment (M) to those at $k=\pi$ and $k=0$, respectively; that is

$$E_G(\pi,\parallel) = E_G^{\parallel}(\mathrm{NS}) = 30\ \mathrm{K}\,,$$

$$E_G(\pi,\perp) = E_G^{\perp}(\mathrm{NS}) = 14\ \mathrm{K}\,,$$

$$E_G(0,\parallel) = E_G^{\parallel}(M) = 14.2\ \mathrm{K}\,,$$

$$E_G(0,\perp) = E_G^{\perp}(M) = 19.5\ \mathrm{K}\,.$$

Three adjustable parameters, $J=44.2$ K, $\alpha=0.12$, and $D=10.6$ K, completely satisfy four independent equations given above. The isotropic gap energy $E_{G0}(\pi) = J(1-\alpha)/2 = 0.44J$ agrees with the predicted value of $0.4J$.[3] The ratio of gaps at $k=\pi$ and $k=0$ in the isotropic limit is given by

$$E_{G0}(0)/E_{G0}(\pi) = (1+\alpha)/(1-\alpha) = 1.3\,.$$

The numerical estimation[10] of this ratio is 2, implying $\alpha=\frac{1}{3}$ in our expression. The value of $J=44.2$ K agrees reasonably well with $J=47$ K determined from the magnetization isotherm. The anisotropy constant $D=10.6$ K is also consistent with our EPR result[11] as well as the analysis of the neutron scattering.[7]

From the experimental finding that the gap at $k=0$ progressively closes with increasing field, while the gap at $k=\pi$ remains constant,[8] it is suggested that the field-dependent gap has the following form:

$$E_G(k,\theta,H) = E_G(k,\theta) - g(\theta)\mu_B SH\cos^2(k/2)\,, \quad (7)$$

where

$$g(\theta) = [(g_{\parallel}\cos\theta)^2+(g_{\perp}\sin\theta)^2]^{1/2}\,.$$

Equation (1) is the special case for $k=0$ in Eq. (7), and the gap at $k=\pi$ is field independent, being in agreement

with the neutron-scattering data. The numerical study[3] shows that in the classical 1D system the gap at $k=0$ opens in proportion to H, while the spectrum is always gapless at $k=\pi$. If this is relevant to the present system, the energy gap of the present system at zero field is considered to be a Zeeman gap created by an effective negative bias field.[12]

The final discussion is concerned with the nature of the field-induced magnetic transition at the critical field. We believe that this system exhibits a transition from the Haldane state with the nonmagnetic singlet ground state to a new ordered phase with the magnetic ground state in the vicinity of H_c. Mixing of the excited triplet states may cause the field-induced phase transition. Since any 1D system with short-range interaction does not undergo phase transition at finite temperature, 3D nature of the interaction is indispensable for the existence of the transition. We speculate that the transition is associated with softening of the massive excitations as in the case of the spontaneous ordering at T_N induced by the interchain interaction.[4] From this point of view, the density of the thermally excited massive excitations, $n_S = \exp[-E_G(H)/kT]$ dominates the magnetization below H_c, giving the exponential dependence of the magnetization curve which is in agreement with the experimental result.

[1]D. M. Haldane, Phys. Lett. **93A**, 464 (1983); Phys. Rev. Lett. **50**, 1153 (1983).

[2]R. Botet, R. Jullien, and M. Kolb, Phys. Rev. B **28**, 3914 (1983).

[3]J. B. Parkinson and J. C. Bonner, Phys. Rev. B **32**, 4703 (1985); J. B. Parkinson, J. C. Bonner, G. Muller, M. P. Nightingale, and H. W. L. Blote, J. Appl. Phys. **57**, 3319 (1985).

[4]I. Affleck, T. Kennedy, E. H. Lieb, and H. Tasaki, Phys. Rev. Lett. **59**, 799 (1987); I. Affleck, Phys. Rev. Lett. **62**, 474 (1989).

[5]W. J. L. Buyers, R. M. Morra, R. L. Armstrong, M. J. Hogan, P. Gerlach, and K. Hirakawa, Phys. Rev. Lett. **56**, 371 (1986); R. M. Morra, W. J. L. Buyers, R. L. Armstrong, and K. Hirakawa, Phys. Rev. B **38**, 543 (1988).

[6]M. Steiner, K. Kakurai, J. K. Kjems, D. Petitgrand, and R. Pynn, J. Appl. Phys. **61**, 3953 (1987).

[7]J. P. Renard, M. Verdaguer, L. P. Regnault, W. A. C. Erkelens, J. Rossat-Mignod, and W. G. Stirling, Europhys. Lett. **3**, 945 (1987).

[8]J. P. Renard, M. Verdaguer, L. P. Regnault, W. A. C. Erkelens, J. Rossat-Mignod, J. Ribas, W. G. Stirling, and C. Vettier, J. Appl. Phys. **63**, 3538 (1988); L. P. Regnault, J. Rossat-Mignod, J. P. Renard, M. Verdaguer, and C. Vettier, Physica (Amsterdam) **156 & 157B**, 247 (1989).

[9]A. Meyer, A. Gleizes, J. J. Gired, M. Verdaguer, and O. Kahn, Inorg. Chem. **21**, 1729 (1982).

[10]D. P. Arovas, A. Auerbach, and F. D. M. Haldane, Phys. Rev. Lett. **60**, 531 (1988).

[11]H. Kikuchi and Y. Ajiro (to be published).

[12]D. C. Mattis, unpublished result quoted by Morra *et al.* (Ref. 5).